

Orientational Ordering of Non-Planar Phthalocyanines on Cu(111): Strength and Orientation of the Electric Dipole Moment

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(Dated: January 19, 2013)

In order to investigate the orientational ordering of molecular dipoles and the associated electronic properties, we studied the adsorption of chlorogallium phthalocyanine molecules (GaClPc, Pc = C₃₂N₈H₁₆⁻²) on Cu(111) using the X-ray standing wave technique, photoelectron spectroscopy, and quantum chemical calculations. We find that for sub-monolayer coverages on Cu(111) the majority of GaClPc molecules adsorb in a 'Cl-down' configuration by forming a covalent bond to the substrate. For bilayer coverages the XSW data indicate a co-existence of the 'Cl-down' and 'Cl-up' configuration on the substrate. The structural details established for both cases and supplementary calculations of the adsorbate system allow us to analyze the observed change of the work function.

PACS numbers: 68.49.Uv, 68.43.Fg, 79.60.Fr

The adsorption of organic semiconductor molecules has been in the focus of numerous experimental and theoretical investigations – many of them addressing the subtle interplay of electronic and structural properties. Early studies [1], which show that the energy levels of organic semiconductor/metal interfaces can exhibit large deviations from the Schottky-Mott relation, conveyed the significance of interface dipoles. Until today and despite the ubiquity of this concept in the field of organic materials, the origin of the interface dipole often remains vague.

To establish a better understanding of the energy level alignment at the interface one should not neglect effects related to the molecular structure of organic adsorbates: Planar molecules such as F₁₆CuPc [2], PTCDA [3, 4] or pentacene derivatives [5], for example, can distort upon adsorption due to the interaction with the substrate and therefore exhibit an induced molecular dipole. Non-planar molecules such as TiOPc [6], SnPc [7–9], SubPc [10, 11] and VOPc [12], which may adsorb in different orientations, form layers with at least partially aligned dipole moments. Hence, for this class of systems the orientational order on the surface is a quantity which strongly influences the interface dipole. In particular, it has been shown that depending on the orientation a layer of molecular dipoles p with an area density N_{dip} can shift the vacuum level (VL) in either direction and, therefore, increase or decrease the work function Φ of the sample according to [13]

$$\Delta\Phi_{\text{dip}} = \pm epN_{\text{dip}}/\epsilon_0\epsilon, \quad (1)$$

where ϵ is the effective dielectric constant of the monolayer. An experimentally and theoretically challenging model system of non-planar organic molecules with a significant dipole moment, for which these effects can be directly studied, is chlorogallium phthalocyanine (GaClPc,

Fig. 1) [14].

In this letter, we present a detailed study on the bonding and orientational ordering of GaClPc on Cu(111) surfaces using the X-ray standing wave (XSW) technique [15], ultra-violet photoelectron spectroscopy (UPS) and density functional theory (DFT) based calculations. While XSW data are taken to determine exact the atomic positions along the surface normal and, thereby, also the orientation of the molecules, the UPS measurements reveal how the adsorbate affects the electronic energy levels. In particular, our results demonstrate that the observed VL shift can be modeled very well if one accounts for the adsorption geometry and the orientation of the molecules.

The XSW experiments were carried out at beamline ID32 of the European Synchrotron Radiation Source

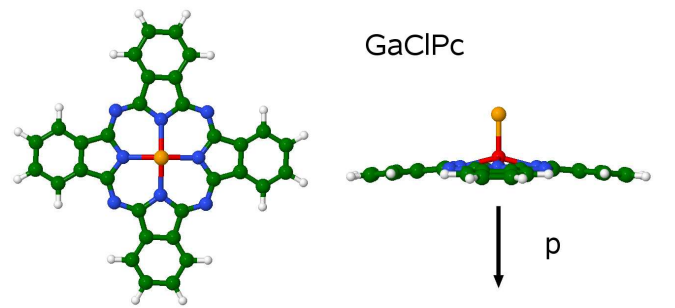


FIG. 1: Structure of the free GaClPc (Pc = C₃₂N₈H₁₆⁻²) molecule as obtained by geometry optimization using the Gaussian03 program package. The results show that the Ga (red) and Cl atoms (orange) are located above the molecular plane with a Ga-Cl bond length of 2.21 Å. The Pc group itself is non-planar with the two inequivalent N species (blue) 0.50 Å and 0.58 Å below the Ga atom.

(ESRF) in Grenoble. Using the (111)-reflection of the copper substrate we have taken data in back-reflection geometry [2, 4], corresponding to the lattice plane spacing $d = 2.08 \text{ \AA}$ with photon energies around $E_{\text{Bragg}} = 2.97 \text{ keV}$. The UPS experiments for different coverages were performed with a photoelectron spectrometer equipped with a standard HeI light source (photon energy 21.2 eV) in our home laboratory. The Cu(111) crystal with a small mosaicity was prepared under ultra-high vacuum conditions by repeated cycles of argon sputtering and annealing (base pressure $4 \times 10^{-10} \text{ mbar}$). The GaClPc material was purchased from Sigma-Aldrich, purified by gradient sublimation, and thoroughly degassed. With a quartz microbalance typical deposition rates of 0.2 \AA/min were realized. For all experiments reported below the substrate temperature was carefully monitored. To model the electronic structure of the molecules on the Cu(111) surface, we employed slab-type DFT based band structure calculations using VASP [16]; more details on the theoretical methods and the chosen geometry are given in the supplementary material [17].

The core-level spectra of GaClPc on Cu(111) show several signals that are suitable for XSW experiments (Fig. 2). By measuring photoemission spectra related to all atomic species in the molecule, namely C(1s), N(1s), Ga(2p_{1/2}), and Cl(2s)/Cl(KLL) Auger, we achieve a detailed electronic and structural characterization of the system.

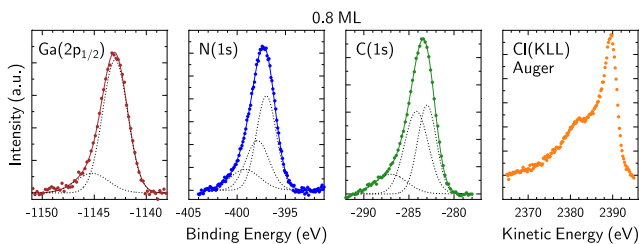


FIG. 2: Background corrected core-level spectra measured with a hemispherical electron energy analyzer for a sub-monolayer of GaClPc on Cu(111). The intensity of the peaks relative to the substrate signal has been used to determine the surface coverage in monolayer equivalent units (ML).

The bonding distances and orientation of the molecule have been derived from the characteristic variation of the photoelectron yield Y_p around the Bragg condition. The XSW data, which can be analyzed according to a well-established procedure using the experimental reflectivity R of the sample, yield two structural parameters: the coherent position P_H and coherent fraction f_H , both of which can be determined by a least-square fitting routine [17]. While P_H gives the average position of the atoms relative to the diffraction planes, f_H yields the spread of positions within the ensemble.

Figure 3 shows XSW results for two different coverages, which were derived from series of core-level spectra.

Unlike planar organic molecules [2, 4], the data corresponding to the different atoms exhibit pronounced differences. For sub-monolayer coverages (0.8 ML, Fig. 3a) our results indicate high orientational order within the molecular ensemble on the surface. To convert the coherent positions given in Fig. 3a, i.e. $P_H(\text{Ga}) = 0.03$, $P_H(\text{C}) = 0.14$, $P_H(\text{N}) = 0.27$, and $P_H(\text{Cl}) = 0.90$, into the (average) bonding distances d_H one must take into account the modulo- d ambiguity of the XSW technique [15]. In principle, two different configurations can be considered for low GaClPc coverages: Either a scenario 'Cl-up' with interatomic distances which deviate strongly from the gas phase structure (e.g. a hypothetical Ga-Cl bond length of only $1.83 \pm 0.07 \text{ \AA}$ compared to 2.21 \AA in the gas phase), or a scenario 'Cl-down' with a corresponding Ga-Cl bond length of $2.33 \pm 0.07 \text{ \AA}$ and a vertical N-Ga distance of 0.50 \AA , i.e. values that are close to the interatomic distances in the gas phase. DFT calculations for the isolated molecule, which show that large molecular distortions of GaClPc are energetically very unfavorable, can be used to rule out the 'Cl-up' case. The obvious conclusion that the molecules adsorb – similar to other Pc derivatives [10, 11] – predominantly in a 'Cl-down' configuration implies that the molecular dipoles contribute with $\Delta\Phi_{\text{dip}} < 0$ to the overall VL shift. Having established the bonding distances for the low coverage (Fig. 3c) with the corresponding error bars (Fig. 3d), we see that the Cu-Cl layer spacing of 1.88 \AA coincides with experimental results for chlorine adsorption on Cu(111) [18]. This agreement suggests a covalent bonding of the Cl atoms to the substrate and, moreover, a hollow adsorption site as reported in Ref. [18].

Complementing this picture, we find increasing magnitudes of f_H for carbon (0.23), nitrogen (0.41), gallium (0.51), and chlorine (0.67), which indicate surprisingly different spatial spreads. Therefore, we studied the influence of thermally activated librational motions of the GaClPc molecules in the 'Cl-down' configuration. Specific model calculations based on a statistical description of the ensemble (presented in the supplementary material [17]) were performed to refine the analysis. The time-averaged spread of positions resulting from our simulations gives XSW parameters f_H and P_H , which – by comparison with the experimental values – allow us to determine the libration amplitude. The analysis shows that the atomic species within the GaClPc molecule are affected very differently and that even for small amplitudes there are strong changes of the coherent fractions for C and N. The relative magnitude of the coherent fractions is consistent with a libration amplitude (rms) of $17 \pm 3^\circ$ around the essentially fixed Cl-atom.

For higher GaClPc coverages (1.4 ML, Fig. 3b) the situation becomes more complex. The relatively small coverage dependence found for the Cl (and Ga) data contrasts with significant changes for the N (and C) signal. In particular the very different values $P_H(\text{N})=0.49$ and

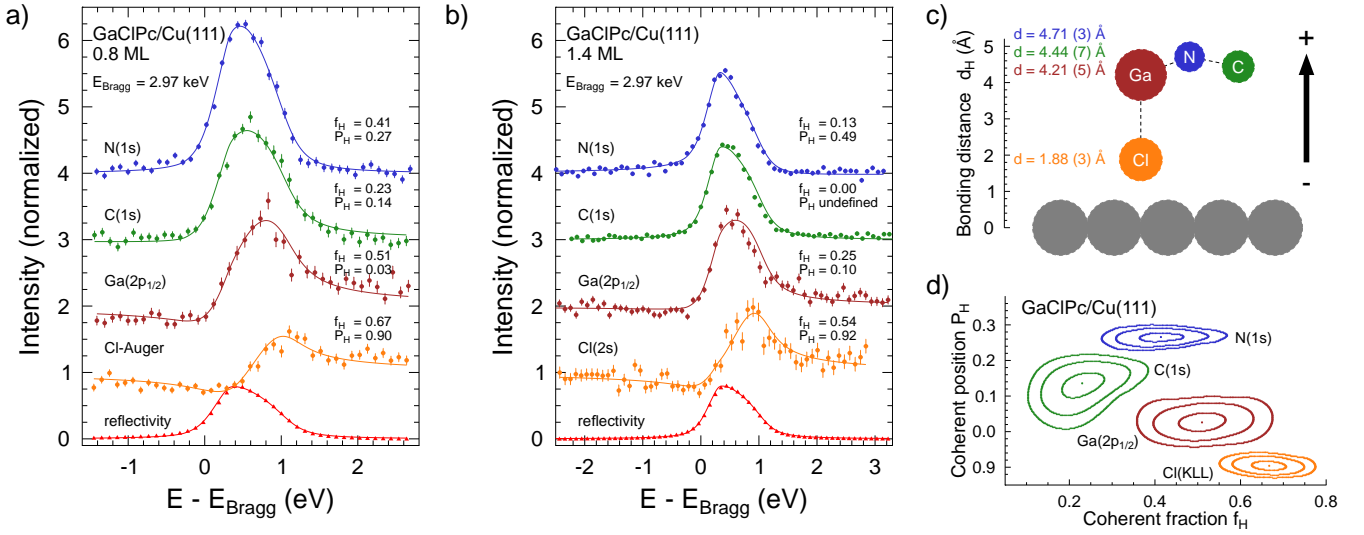


FIG. 3: (a),(b) XSW data for GaClPc on Cu(111) taken for two different coverages in back-reflection geometry at elevated temperature. The photon energy has been scanned around $E_{\text{Bragg}} = 2.97$ keV to measure the photoelectron yield (circles) and reflectivity (triangles). Least-square fits to the data (solid lines) give the coherent fraction f_H and coherent position P_H that are related to the adsorption geometry. (c) Average bonding distances d_H for GaClPc as derived from the data in (a). (d) χ^2 -confidence map for fits to the XSW data in (a). The 1 σ -, 2 σ -, and 3 σ -contour levels show the statistical significance of the data analysis [4].

$f_H(\text{N})=0.13$ for nitrogen cannot be explained with only one molecular orientation. Model calculations, which take into account that the XSW parameter f_H and P_H refer to a coherent average over all inequivalent sites in the bilayer [15], i.e.

$$f_H e^{2\pi i P_H} = \frac{1}{N} \sum_{k=1}^N \left(e^{2\pi i \Delta_k^{\text{down}}/d} + e^{2\pi i \Delta_k^{\text{up}}/d} \right), \quad (2)$$

($\Delta_k^{\text{down/up}}$ denoting the position of the k^{th} atom relative to the substrate lattice), indicate a co-existence of 'Cl-up' and 'Cl-down' configurations on the surface. The adsorption of GaClPc molecules with opposite orientation in the second layer – a phenomenon reported also for other Pc derivatives [6, 9] – could be confirmed also by metastable atom electron spectroscopy (MAES) measurements [19]. Within our coverage series, we verified that a deposition of more than 4 ML results in atomically disordered systems with incoherent XSW signals ($f_H = 0$) for all elements.

In order to study how the orientational order of the molecules affects the VL shift we measured the work function of the system for increasing GaClPc coverage (Fig. 4a). At first, the results obtained from the photoemission spectra reveal a rapid decrease below 0.2 ML as expected for the 'Cl-down' configuration. The continuous, yet slightly retarded VL shift results in a minimum of $\Delta\Phi = -0.34$ eV at the monolayer coverage. To overcome possible kinetic limitations we deposited more material (resulting in a gradual increase of Φ for coverages of more than 1 ML due to preferential 'Cl-up' nucle-

ation) and applied a short annealing of the multilayer at 300 °C. This procedure yields a coverage of slightly less than 1 ML and a shift of $\Delta\Phi = -0.60$ eV. Because DFT calculations, which we have performed using the adsorption geometry shown in Fig. 3c, predict a similar decrease of $\Delta\Phi = -0.55$ eV for a comparable coverage, we may relate the electronic properties of annealed monolayer to the low-coverage XSW data. Due to the orientational order we can separate the total change $\Delta\Phi$ into two contributions with

$$\Delta\Phi = \Delta\Phi_{\text{dip}} + \Delta\Phi_{\text{bond}}. \quad (3)$$

Thus, we distinguish $\Delta\Phi_{\text{dip}}$, which is related to the dipole moment of the molecules according to Eq. (1), and $\Delta\Phi_{\text{bond}}$, which contains the effect of the molecule-metal interaction. To quantify the dipole contribution we have calculated a monolayer of GaClPc without metal substrate. Again using the adsorption geometry shown in Fig. 3c we obtain $\Delta\Phi_{\text{dip}} = -0.30$ eV. Because of the large substrate-Pc distance and the correspondingly small Pauli repulsion the associated value $\Delta\Phi_{\text{bond}} = -0.25$ eV essentially reveals the effect of the charge rearrangement within the Ga-Cl group and between the Cl and Cu atoms [17].

These conclusion are corroborated by the interpretation of the valence band spectra shown in Fig. 4b. The data obtained for different coverages show that neither before nor after the annealing procedure prominent interface states – as they were reported for the adsorption of other planar [20] and non-planar [21] Pc molecules directly below the Fermi energy – can be observed. This

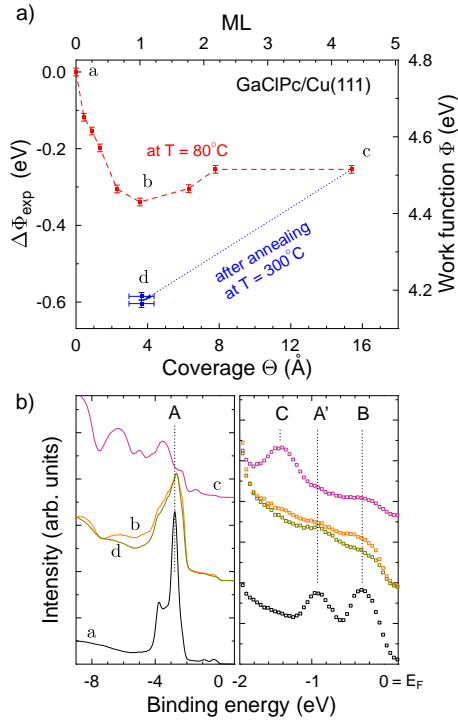


FIG. 4: (a) Coverage dependent work function of GaClPc on Cu(111). (b) Valence band region measured by UPS for coverages labeled correspondingly in the top panel. In these spectra peak A belongs to the Cu 3d band, A' is a satellite of A due to excitation by parasitic He I β radiation, peak B is the Shockley surface state of the clean Cu(111), and peak C is the HOMO-derived state of the multilayer film.

absence of characteristic spectral features in the HOMO-LUMO gap [22] illustrates the weak interaction between the substrate and the Pc ring in the 'Cl-down' orientation. We note that due to the photoemission selection rules and the orientation of the molecules no HOMO-derived states can be seen in the normal emission spectra of both monolayer films shown Fig. 4b – in contrast to the disordered multilayer film, which exhibits a pronounced HOMO-related peak centered at -1.42 eV. Moreover, the spectra illustrate the non-ideal growth of GaClPc at 80°C and the significant re-ordering caused by the annealing procedure. The strong quenching of the Shockley surface state, which we find for the annealed film, clearly indicates a more uniform substrate coverage.

In summary, the XSW data together with the UPS measurements and the DFT calculations give a conclusive picture of the molecules' orientation and bonding. For sub-monolayer coverages at sufficiently high substrate temperature the vast majority of GaClPc molecules adsorb in the 'Cl-down' configuration with a Cl-Cu layer spacing of 1.88 \AA that indicates covalent bonding of the chlorine atoms. The interaction with the substrate gives rise to subtle deviations from the gas phase structure: In agreement with the DFT calculations [17], the Ga-Cl

bond length of 2.33 \AA measured by XSW is slightly larger than in the gas phase, while the average position of the carbon atoms in the experiment and the calculations indicates a certain bending of the molecule [17]. Moreover, the coherent fractions observed in the experiment can be related to thermal librations of the molecules. Due to the orientational order the molecular dipoles contribute significantly to the vacuum level shift and the resulting interface dipole. Detailed calculations for the annealed monolayer support this conclusion quantitatively with $\Delta\Phi_{\text{dip}} = -0.30\text{ eV}$. The influence of intermolecular interactions is demonstrated by the coexistence of 'Cl-down' and 'Cl-up' configurations found for deposition at 80°C . Interestingly, a subsequent annealing allows a controlled re-ordering of the molecular dipoles and a change of the corresponding electronic properties. Furthermore, we believe that the adsorption behavior of GaClPc and its impact on the electronic structure represent important characteristics of non-planar organic molecules.

We thank N. Koch and J. Pflaum for stimulating interactions, T. Suzuki and H. Machida for experimental support. We gratefully acknowledge the ESRF for providing excellent facilities, the DFG (Tübingen), the G-COE (Chiba), and the FWF (Graz) for funding our work.

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 - [22] HOMO (LUMO): highest occupied (lowest unoccupied) molecular orbital